



Supplement of

On the sources and sinks of atmospheric VOCs: an integrated analysis of recent aircraft campaigns over North America

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6 **Table S1. Gas-phase species and instrumentation used here.**

Campaign	Species involved in this work	Measurement technique	Measurement reference
CalNex	isoprene, monoterpenes, benzene, toluene, C8 aromatics methanol, acetone, methyl ethyl ketone, formaldehyde, acetaldehyde, MVK+MACR acetonitrile	PTR-MS	de Gouw and Warneke (2007)
	2-BuONO ₂ , 3-PenONO ₂ , 2-PenONO ₂ , 3-methyl-2-BuONO ₂ C ₂ H ₆ , C ₃ H ₈ , i-butane, n-butane, i-pentane, n-pentane, n-hexane, n-heptane, n-octane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, C ₂ H ₄ , propene, 1-butene, trans-2-butene, cis-2-butene, C ₂ H ₂	WAS	Colman et al. (2001), Schauffler et al. (2003)
	PAN	CIMS	Zheng et al. (2011), Osthoff et al. (2008)
	NO, NO ₂ , NO _y	Gas-phase chemiluminescence	Pollack et al. (2010), Ryerson et al. (1999), Ryerson et al. (1998)
DC3 DC-8	isoprene, monoterpenes, benzene, toluene, xylene methanol, acetone, acetaldehyde, MVK+MACR acetonitrile	PTR-MS	Wisthaler et al. (2002)
	formaldehyde	DFGAS (base)	Richter et al. (2015), Weibring et al. (2010)
	formaldehyde	ISAF-LIF (sens)	Cazorla et al. (2015), DiGangi et al. (2011), Hottle et al. (2009)
	ISOPOOH+IEPOX, glycolaldehyde, hydroxyacetone, peroxyacetic acid, CH ₃ OOH ISOPN, PROPNN	CIT-CIMS (CF ₃ O ⁻)	Crounse et al. (2006), St Clair et al. (2010)
	2-BuONO ₂ , 3-methyl-2-BuONO ₂ , 3-PenONO ₂ , 2-PenONO ₂ C ₂ H ₆ , C ₃ H ₈ , i-butane, n-butane, i-pentane, n-pentane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, n-hexane, n-heptane, 2,4- dimethylpentane, 2-methylhexane, 2,3-dimethylpentane, 3-methylhexane, 2,2,4-trimethylpentane, C ₂ H ₄ , propene, trans-2-butene, cis-2-butene, cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, C ₂ H ₂	WAS	Blake et al. (2003)
	PAN, PPN	CIMS	Huey (2007), Kim et al. (2007), Slusher et al. (2004)
	MPN	TD-LIF	Wooldridge et al. (2010)
	NO, NO ₂ , NO _y	Gas-phase chemiluminescence	Pollack et al. (2010), Ryerson et al. (1999), Ryerson et al. (1998)
			Apel et al. (2010)
DC3 GV	i-butane, n-butane, i-pentane, n-pentane, n-hexane, n-heptane, benzene, toluene, ethylbenzene+m,p-xylene, o-xylene, isoprene, alpha-pinene, camphene, beta-pinene, limonene methanol, ethanol, methyl butenol, acetone, MEK, propanal, butanal, acetaldehyde, MVK, MACR acetonitrile	TOGA	
	formaldehyde	CAMS	Fried et al. (2011)
	CH ₃ OOH	PCIMS	O'Sullivan et al. (2018)
	NO, NO ₂	Gas-phase chemiluminescence	Weinheimer et al. (1994)
SENEX	isoprene, monoterpenes, benzene, toluene, xylene methanol, acetone, methyl ethyl ketone, acetaldehyde, MVK+MACR acetonitrile	PTR-MS	de Gouw and Warneke (2007)
	C ₂ H ₆ , C ₃ H ₈ , i-butane, n-butane, i-pentane, n-pentane, n-hexane, C ₂ H ₄ , propene, C ₂ H ₂	WAS	Lerner et al. (2017), Gilman et al. (2009)
	formaldehyde	ISAF-LIF	Cazorla et al. (2015), DiGangi et al. (2011), Hottle et al. (2009)
	ISOPOOH+IEPOX ISOPN, MVKN+MACRN HCOOH, C ₂ H ₄ O ₃ , C ₃ H ₄ O ₃ , C ₃ H ₄ O ₄ , C ₃ H ₈ O ₄ , C ₉ H ₁₄ O ₄ , C ₁₀ H ₁₆ O ₃	UW CIMS (sens)	Lee et al. (2014)
	HCOOH	NOAA CIMS (base)	
	glyoxal	ACES	Min et al. (2016)

	PAN, PPN	CIMS	_ENREF_28, Zheng et al. (2011), Osthoff et al. (2008), Slusher et al. (2004)
	NO, NO ₂ , NO _y	Gas-phase chemiluminescence	Pollack et al. (2010), Ryerson et al. (1999), Ryerson et al. (1998)
SEAC ⁴ RS	isoprene, monoterpenes, benzene, toluene methanol, acetone, acetaldehyde, MVK+MACR acetonitrile	PTR-MS	Wisthaler et al. (2002)
	formaldehyde	CAMS (base)	Fried et al. (2011)
	formaldehyde	ISAF-LIF (sens)	Cazorla et al. (2015), DiGangi et al. (2011), Hottle et al. (2009)
	ISOPOOH+IEPOX, hydroxyacetone, peroxyacetic acid ISOPN, PROPNN, MVKN+MACRN C ₄ O ₄ H ₇ N, C ₅ O ₅ H ₉ N, BUTENE HN	CIT-CIMS (CF ₃ O ⁻)	Crounse et al. (2006), St Clair et al. (2010)
	2-BuONO ₂ , 3-methyl-2-BuONO ₂ , 3-PenONO ₂ , 2-PenONO ₂ C ₂ H ₆ , C ₃ H ₈ , i-butane, n-butane, i-pentane, n-pentane, neopentane, n- hexane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, n- heptane, C ₂ H ₄ , propene, trans-2-butene, cis-2-butene, 1-butene, i-butene, 1-pentene, C ₂ H ₂	WAS	Blake et al. (2003)
	PAN, PPN	PAN-CIMS	Huey (2007), Kim et al. (2007), Slusher et al. (2004)
	MPN	TD-LIF	Wooldridge et al. (2010)
	NO, NO ₂ , NO _y	Gas-phase chemiluminescence	Pollack et al. (2010), Ryerson et al. (1999), Ryerson et al. (1998)
DISCOVER- AQ	formaldehyde	DFGAS	Richter et al. (2015), Weibring et al. (2010)
	non-methane VOCs	PTR(-ToF-)MS	Müller et al. (2016), Müller et al. (2014)
	ethane (DISCOVER-AQ CO)	TILDAS	Yacovitch et al. (2014)
	NO, NO ₂ , NO _y	Gas-phase chemiluminescence	Weinheimer et al. (1994)
FRAPPÉ	formaldehyde, ethane	CAMS	Fried et al. (2011)
	monoterpenes, acetonitrile methanol, acetaldehyde, acetone, isoprene, MVK+MACR, methyl ethyl ketone, benzene, toluene, C8 aromatics	PTR-MS (sens)	Kaser et al. (2013)
	methanol, acetaldehyde, acetone, isoprene, MVK, MACR, methyl ethyl ketone, benzene, toluene, ethylbenzene-m-p-xylene+o-xylene ethanol, propanal, butanal, methyl butenol C ₃ H ₈ , i-butane, n-butane, i-pentane, n-pentane, n-hexane, 2-methylpentane, 3-methylpentane, n-heptane tert-butyl nitrate, 2-butyl nitrate-n-butyl nitrate, 2-pentyl nitrate-3- pentyl nitrate	TOGA (base)	Apel et al. (2010)
	CH ₃ OOH, HCOOH, Acetic acid	PCIMS	Treadaway et al. (2018)
	C ₂ H ₄ , propene, cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, C ₂ H ₂	WAS	Blake et al. (2003)
	PAN, PPN	PAN-CIMS	Zheng et al. (2011)
	NO, NO ₂	Gas-phase chemiluminescence	(Weinheimer et al. (1994))

Table S2. Sensitivity of spatially aggregated model performance for total VOC-carbon to the use of data from alternate instruments for co-measured VOCs.

	Base case ^a	DC3 LIF HCHO	SEAC4RS LIF HCHO	SENEX UW CIMS HCOOH	FRAPPÉ PTRMS VOCs	All
NMB						
FT (>3km)	-63.7%	-62.0%	-63.8%	-63.7%	-63.7%	-62.1%
PBL (<2km)	-37.2%	-36.3%	-37.3%	-37.2%	-37.3%	-36.3%
R ²						
FT (>3km)	0.066	0.097	0.067	0.065	0.066	0.098
PBL (<2km)	0.361	0.445	0.362	0.369	0.360	0.449

^aBase case uses DC3 DFGAS HCHO, SEAC4RS CAMS HCHO, SENEX NOAA CIMS HCOOH, FRAPPÉ TOGA methanol, acetaldehyde, acetone, isoprene, MVK, MACR, MEK, benzene, toluene, C8 aromatics.

Table S3. Sensitivity of spatially aggregated model performance for total VOC reactivity to the use of data from alternate instruments for co-measured VOCs.

	Base case ^a	DC3 LIF HCHO	SEAC4RS LIF HCHO	SENEX UW CIMS HCOOH	FRAPPÉ PTRMS VOCs	All
NMB						
FT (>3km)	-62.6%	-61.9%	-63.2%	-62.6%	-62.6%	-62.5%
PBL (<2km)	-33.9%	-32.7%	-34.0%	-33.7%	-33.9%	-32.8%
R ²						
FT (>3km)	0.043	0.045	0.046	0.043	0.043	0.048
PBL (<2km)	0.542	0.629	0.542	0.547	0.542	0.631

^aBase case uses DC3 DFGAS HCHO, SEAC4RS CAMS HCHO, SENEX NOAA CIMS HCOOH, FRAPPÉ TOGA methanol, acetaldehyde, acetone, isoprene, MVK, MACR, MEK, benzene, toluene, C8 aromatics.

Table S4. Sensitivity of campaign-aggregated mixing ratio and model bias to the use of data from alternate instruments for co-measured VOCs

		PBL			FT		
		Mixing ratio (ppbC)	Model bias (ppbC)	Model bias (%)	Mixing ratio (ppbC)	Model bias (ppbC)	Model bias (%)
Formaldehyde	base	1.930	-0.401	-22.6	0.230	-0.048	-27.8
	sens	1.944	-0.424	-23.3	0.250	-0.072	-36.9
Formic acid	base	1.006	-0.721	-76.4	0.430	-0.330	-86.3
	sens	0.972	-0.709	-75.8	0.244	-0.153	-73.5
Methanol	base	4.238	-2.135	-59.9	1.299	-0.924	-77.7
	sens	4.191	-2.062	-58.8	1.303	-0.927	-77.7
Acetaldehyde	base	1.162	-0.545	-57.3	0.185	-0.156	-91.0
	sens	1.212	-0.580	-59.3	0.186	-0.159	-91.1
Acetone	base	6.671	-2.150	-34.7	3.459	-1.761	-52.3
	sens	6.803	-2.272	-36.0	3.466	-1.776	-52.4
Isoprene	base	0.259	-0.116	-74.1	0.019	-0.018	-100.0
	sens	0.309	-0.155	-78.1	0.020	-0.019	-100.0
MVK+MACR	base	0.424	-0.165	-58.5	0.035	-0.031	-99.7
	sens	0.450	-0.177	-58.5	0.035	-0.031	-99.7
MEK	base	0.636	0.240	43.4	0.167	-0.077	-75.5
	sens	0.697	0.187	34.9	0.168	-0.078	-76.4
Benzene	base	0.291	-0.095	-38.9	0.108	-0.073	-72.9
	sens	0.298	-0.105	-40.6	0.108	-0.074	-73.0
Toluene	base	0.210	0.041	13.6	0.026	-0.021	-97.8
	sens	0.221	0.039	8.6	0.026	-0.021	-97.8
Xylene	base	0.112	-0.039	-59.5	0.014	-0.013	-100.0
	sens	0.126	-0.052	-62.9	0.015	-0.015	-100.0

Table S5. Sensitivity of campaign-aggregated reactivity and model bias to the use of data from alternate instruments for co-measured VOCs

		PBL			FT		
		Reactivity (s ⁻¹)	Model bias (s ⁻¹)	Model bias (%)	Reactivity (s ⁻¹)	Model bias (s ⁻¹)	Model bias (%)
Formaldehyde	base	0.343	-0.071	-22.6	0.023	-0.004	-26.7
	sens	0.346	-0.076	-23.3	0.026	-0.007	-35.8
Formic acid	base	0.009	-0.006	-76.4	0.003	-0.002	-86.3
	sens	0.009	-0.006	-75.8	0.002	-0.001	-73.5
Methanol	base	0.080	-0.039	-59.2	0.010	-0.008	-77.2
	sens	0.080	-0.038	-58.2	0.010	-0.008	-77.2
Acetaldehyde	base	0.191	-0.087	-57.4	0.018	-0.015	-90.7
	sens	0.198	-0.093	-59.3	0.018	-0.016	-90.8
Acetone	base	0.008	-0.003	-34.6	0.002	-0.001	-52.1
	sens	0.008	-0.003	-36.0	0.002	-0.001	-52.3
Isoprene	base	0.111	-0.050	-74.1	0.006	-0.005	-100.0
	sens	0.130	-0.066	-78.1	0.006	-0.005	-100.0
MVK+MACR	base	0.052	-0.021	-58.5	0.003	-0.003	-99.7
	sens	0.055	-0.022	-58.2	0.003	-0.003	-99.7
MEK	base	0.004	0.001	40.6	0.001	-0.000	-72.3
	sens	0.005	0.001	34.7	0.001	-0.000	-73.2
Benzene	base	0.001	-0.000	-38.1	0.000	-0.000	-73.3
	sens	0.001	-0.000	-40.6	0.000	-0.000	-73.4
Toluene	base	0.004	0.001	13.7	0.000	-0.000	-97.7
	sens	0.004	0.001	8.6	0.000	-0.000	-97.8
Xylene	base	0.007	-0.002	-59.5	0.001	-0.000	-100.0
	sens	0.008	-0.003	-62.9	0.001	-0.001	-100.0

Table S6. Correlation between observed OVOCs and model-derived biogenic (\mathcal{B}_{OVOC}) and anthropogenic (\mathcal{A}_{OVOC}) contributions.

	SEAC ⁴ RS	SENEX	DISCOVER-AQ TX	Other campaigns
Acetaldehyde	0.71	0.62	0.65	
Formaldehyde	0.71	0.71	0.63	
Acetone	0.87	0.70	0.68	
MEK	n/a	0.68	0.62	
PAA	0.85	n/a	n/a	
Methanol	0.55	0.73	0.53	
MVK	0.74	0.75	0.82	<0.50
MACR	0.75	0.75	0.78	
HCOOH	n/a	0.79	n/a	
Acetic acid	n/a	n/a	0.44	
Glyoxal	n/a	0.79	n/a	
Glycolaldehyde	n/a	n/a	0.63	
Hydroxyacetone	0.80	n/a	n/a	

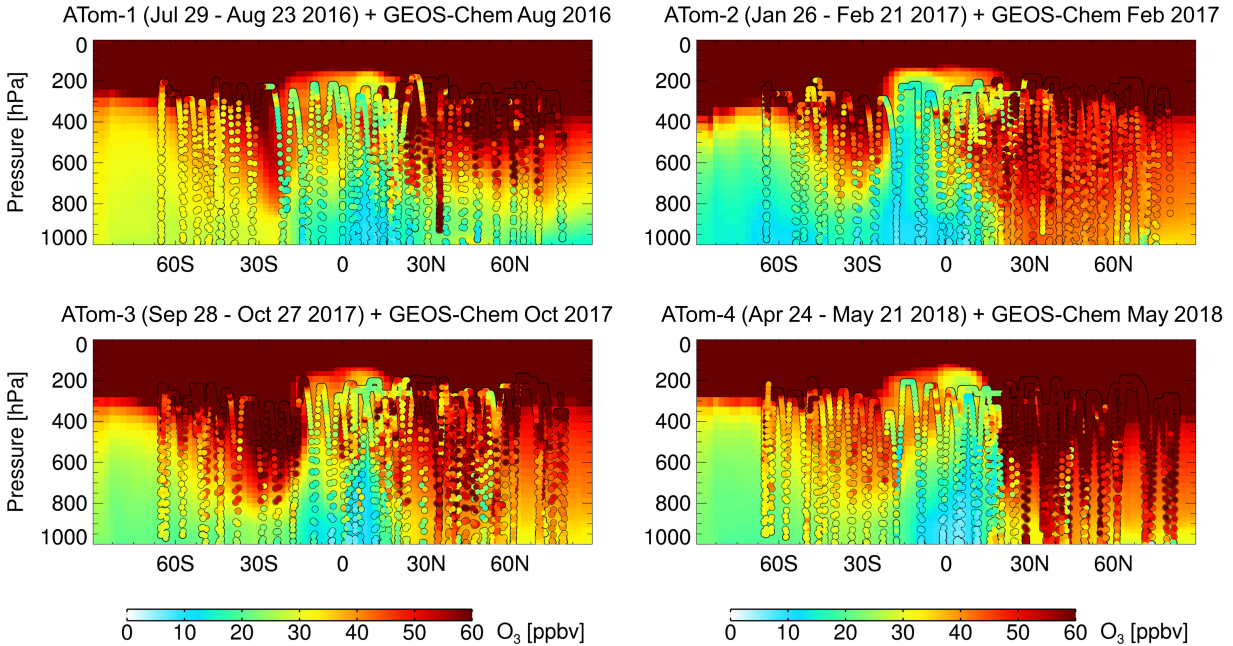


Figure S1. Ozone over the Pacific Ocean. Colored circles show airborne observations from the Atmospheric Tomography Mission (ATom) (Wofsy et al., 2018) within 100°W-170°E. Plotted in the background is the monthly mean ozone curtain simulated by GEOS-Chem (global simulation at 2°×2.5°) at ~177.5°W for the corresponding month.

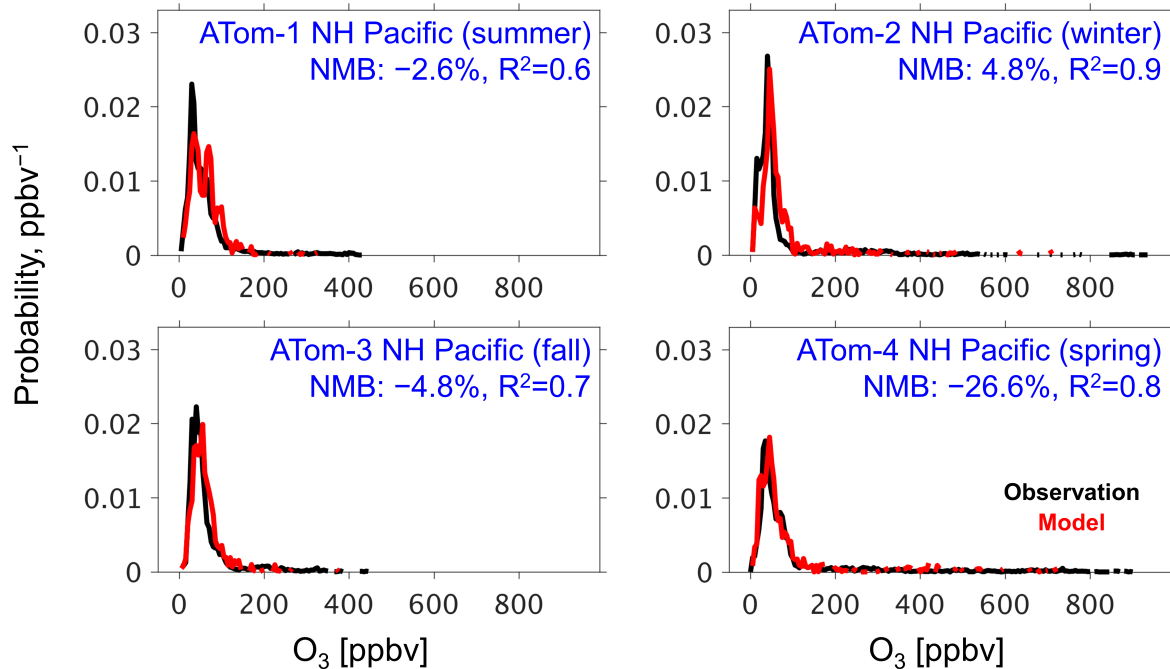
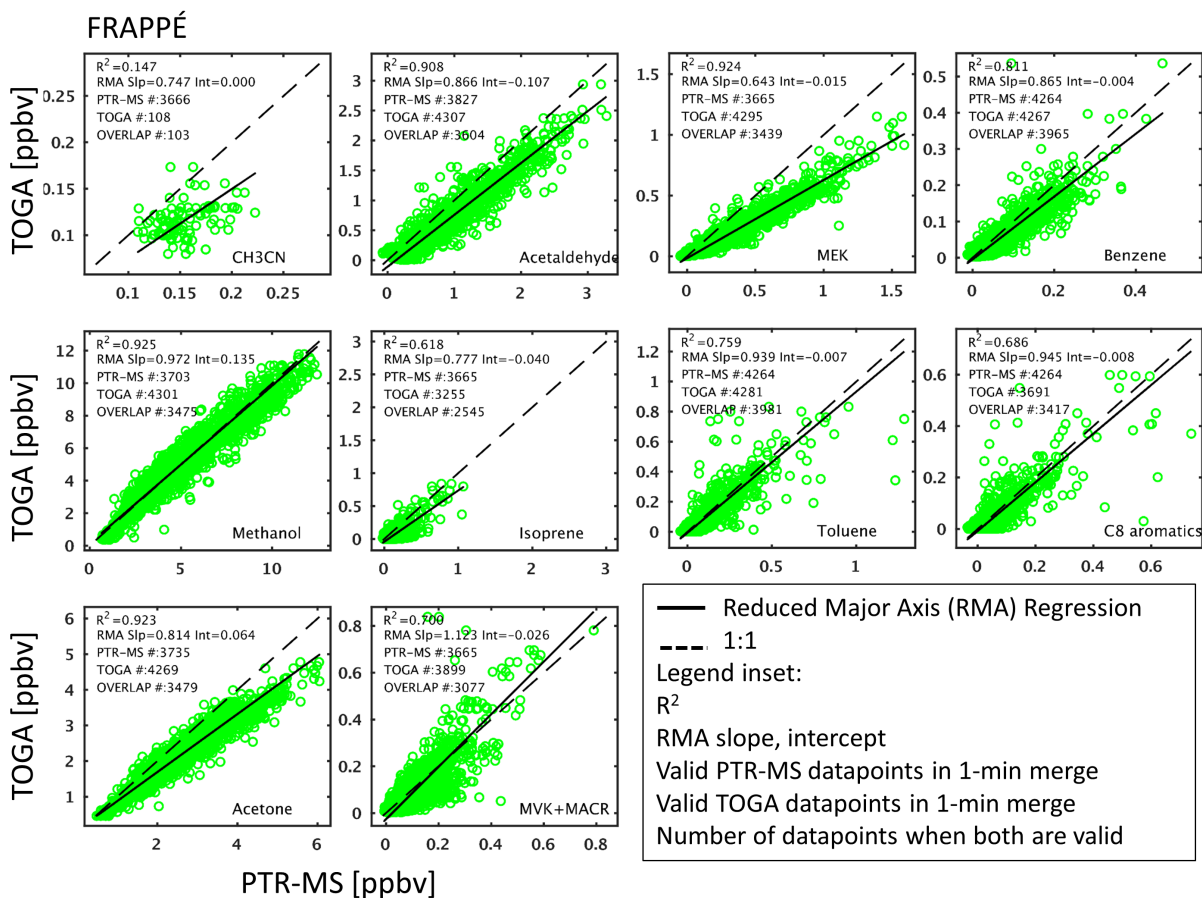
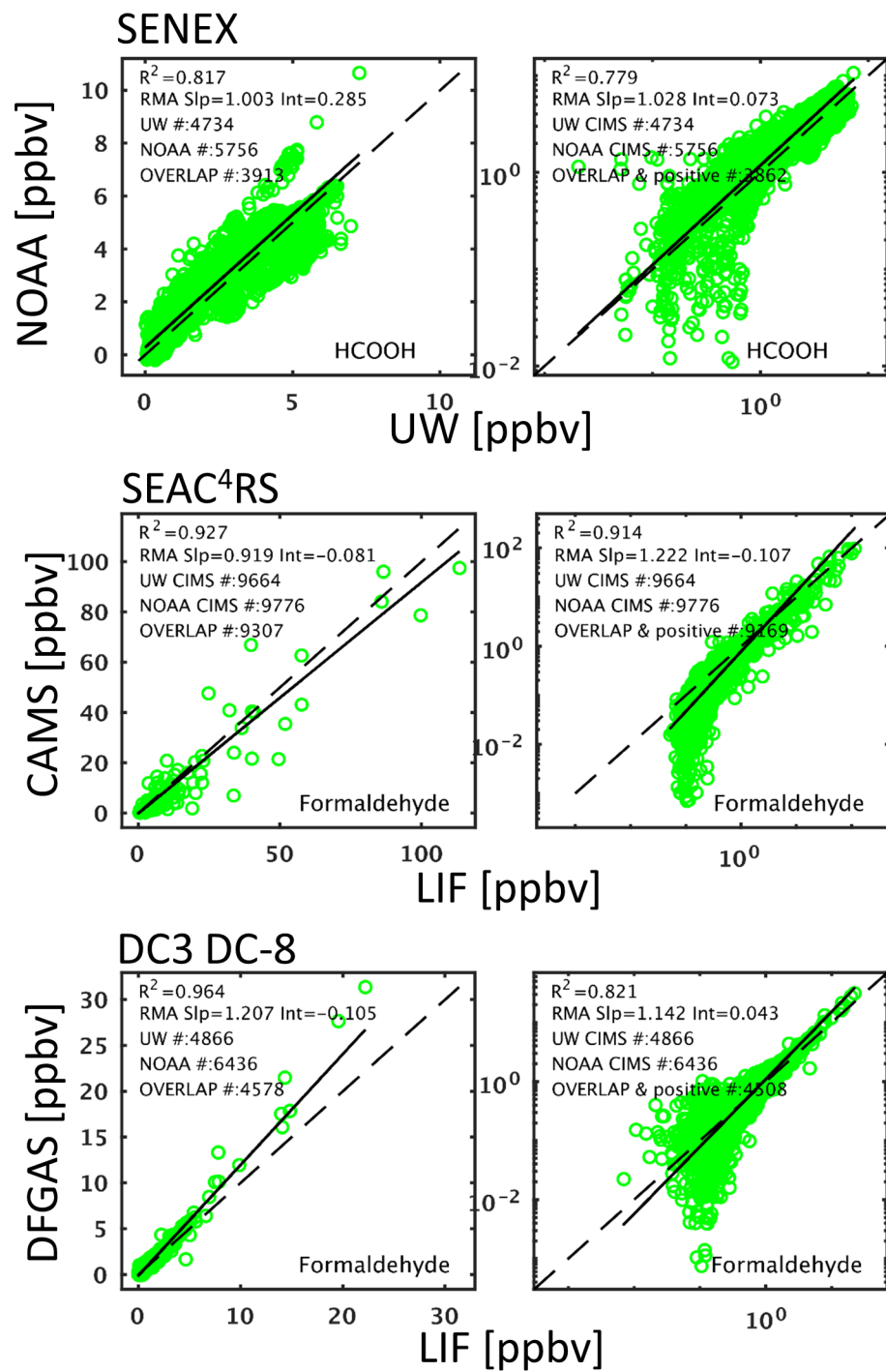


Figure S2. Ozone probability density functions over the northern Pacific (100°W-170°E, 0°-90°N). Plotted are ATom observations (black) and co-located GEOS-Chem model predictions (red), with correlations and normalized mean biases given inset.



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37 **Figure S3. Inter-comparison of co-measured VOCs from FRAPPÉ.**



38

39 **Figure S4. Inter-comparison of concurrent HCOOH measurements during SENEX and of concurrent**
 40 **formaldehyde measurements during DC3 DC-8 and SEAC⁴RS. See legends in Figure S18.**

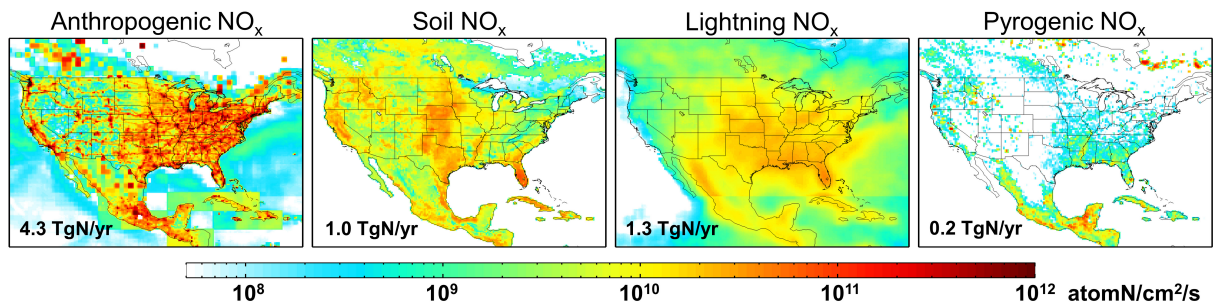


Figure S5. Annual NO_x emissions fluxes over North America as simulated by GEOS-Chem for 2013.

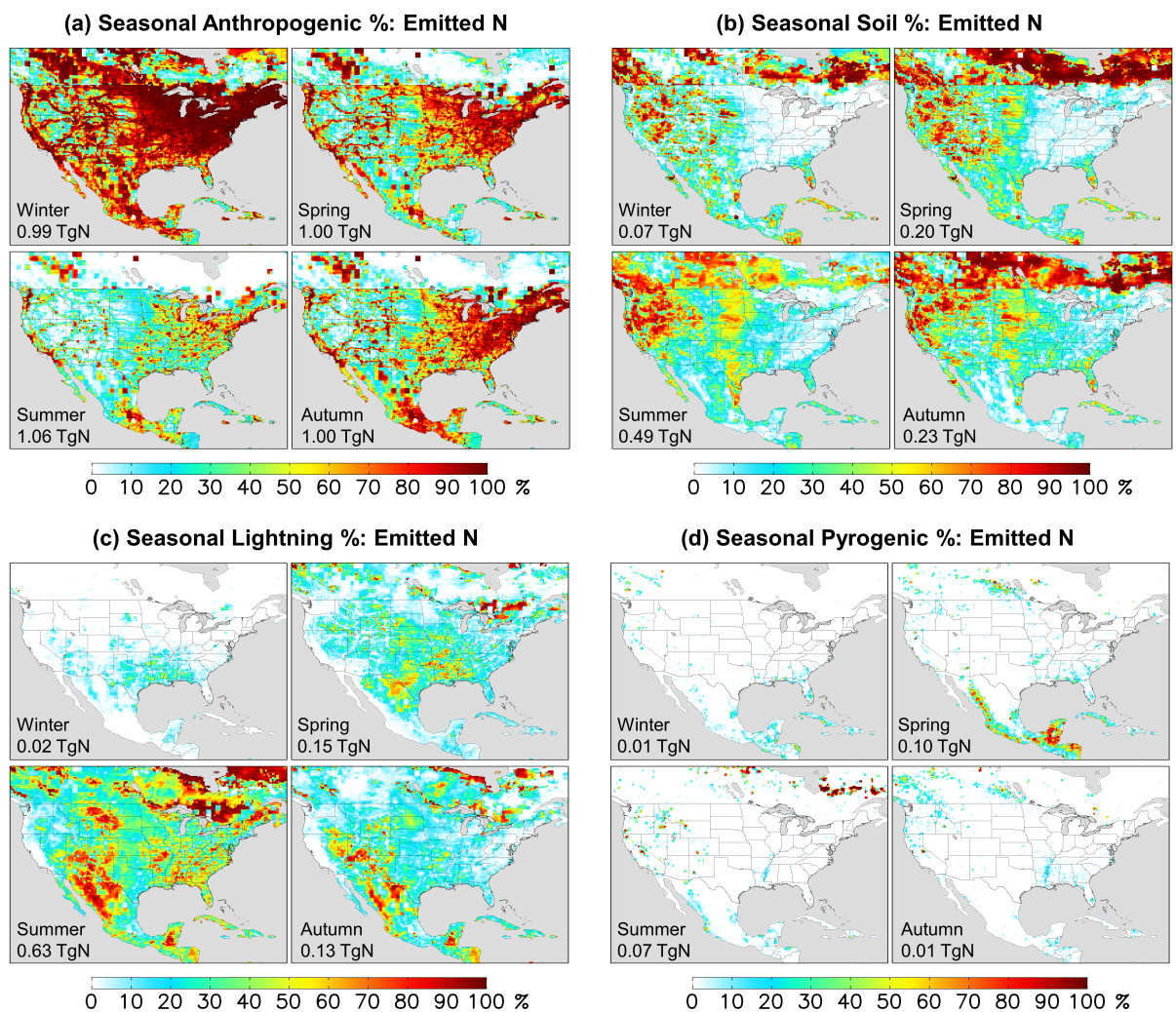


Figure S6. Seasonal contribution of each emission sector to total modeled NO_x emissions.

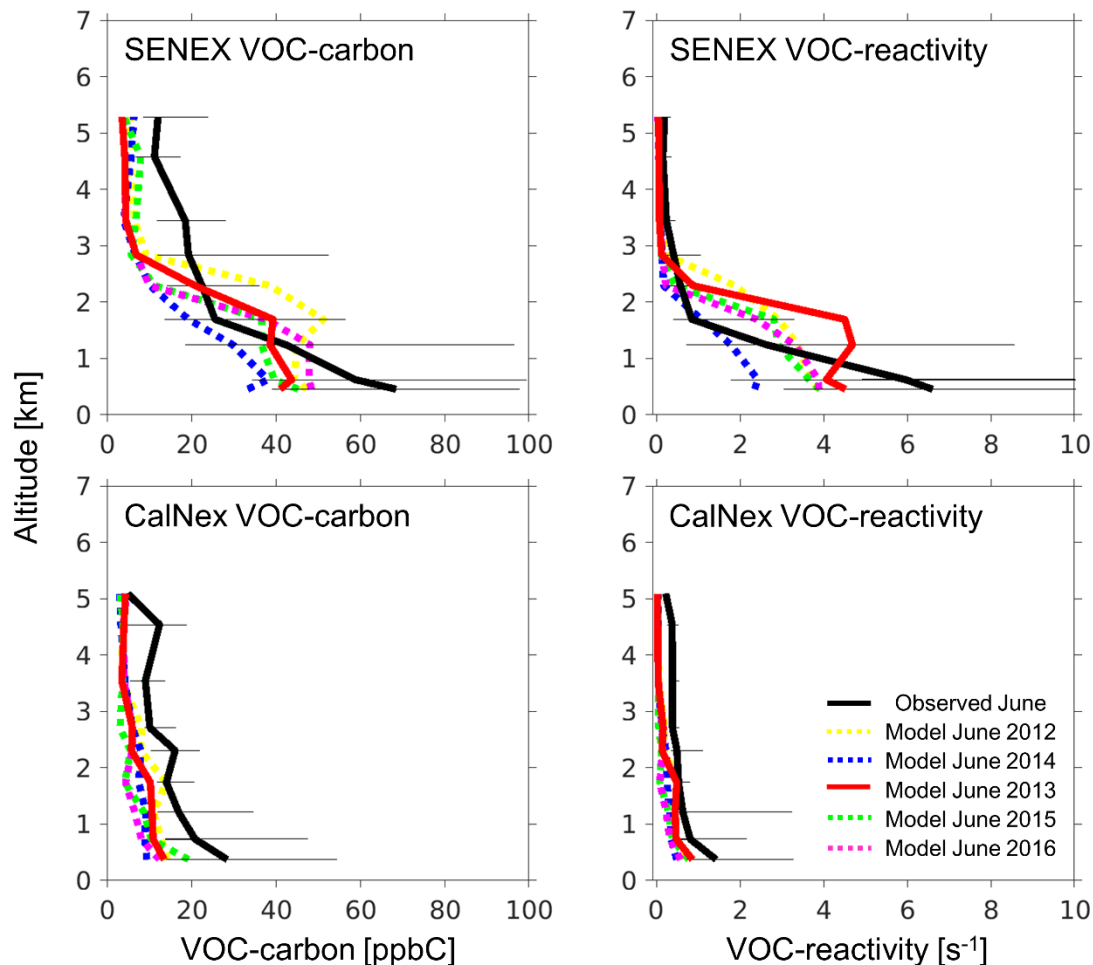


Figure S7. Vertical VOC-carbon and reactivity profiles as measured in 2013 and simulated by GEOS-Chem for June of 2012-2016 along the SENEX and CalNex aircraft flight tracks. Plotted are the observed (solid black lines) and predicted (2013: solid red lines; other years: dashed lines) median profiles, with horizontal bars indicating the 5th-95th percentiles measured for each vertical bin. Bin resolution is 0.5km below 3km and 1km above 3km. VOCs included in the profile correspond to the species shown in Fig. S17 (CalNex) and S18 (SENEX).

Given the range in measurement years spanned by the aircraft measurements, we performed a set of one-month simulations spanning 5 different years (June for 2012-2016) to assess the potential impact of interannual variability on these findings. Results are shown in Fig. S1 for the CalNex and SENEX flight tracks. In both cases the model-measurement VOC-C differences are highly consistent across years. We see a higher degree of interannual variability for VOC-reactivity over the SENEX domain, reflecting year-to-year differences in biogenic VOC emissions over this region. However, the key features of the comparison (a model underestimate near-surface, overly-flat vertical profile within the PBL, and strong FT underestimate) are consistent between our simulation year (2013) and the other four years.

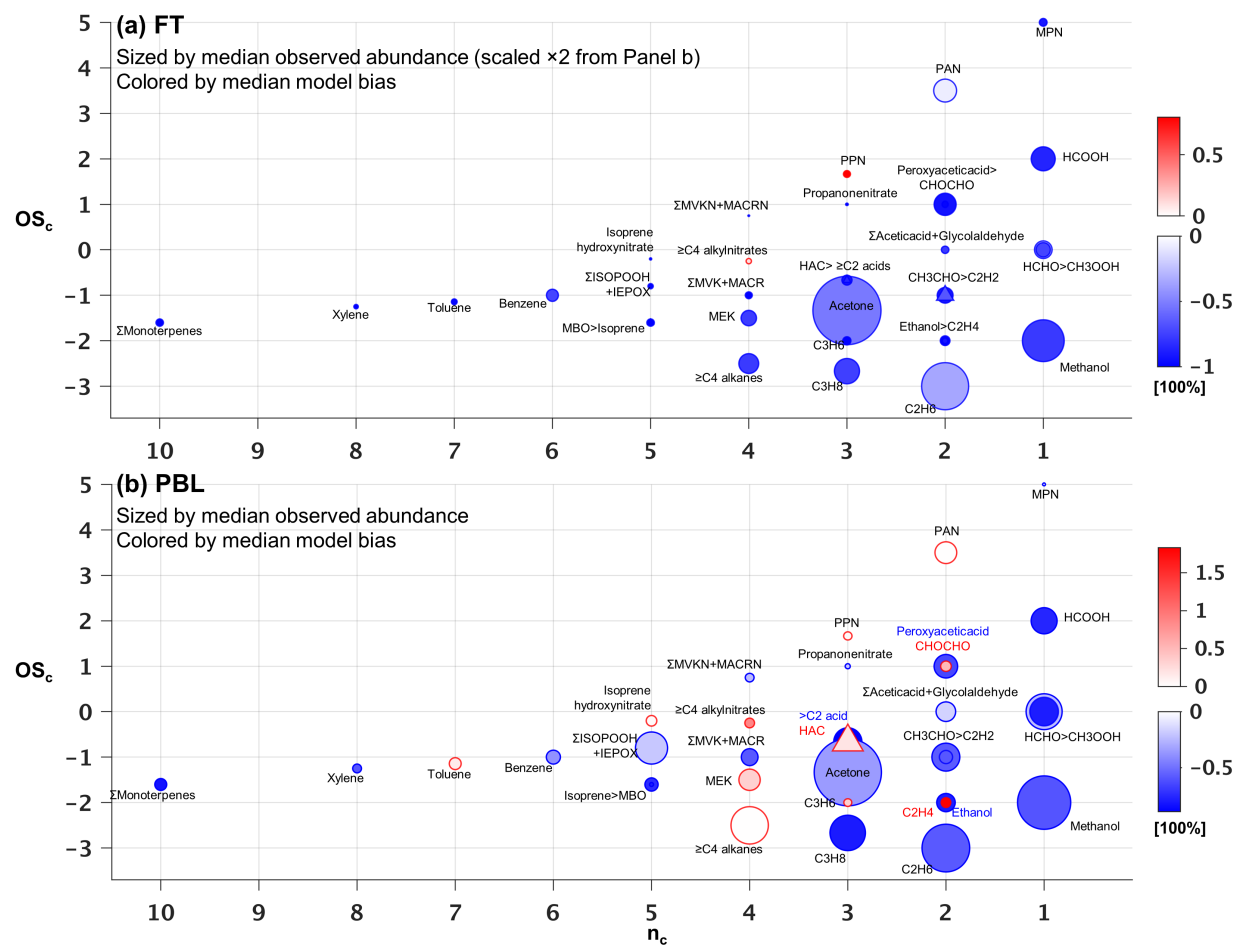


Figure S8. Same as Figure 5, but with the color shaded indicating the median relative model bias.

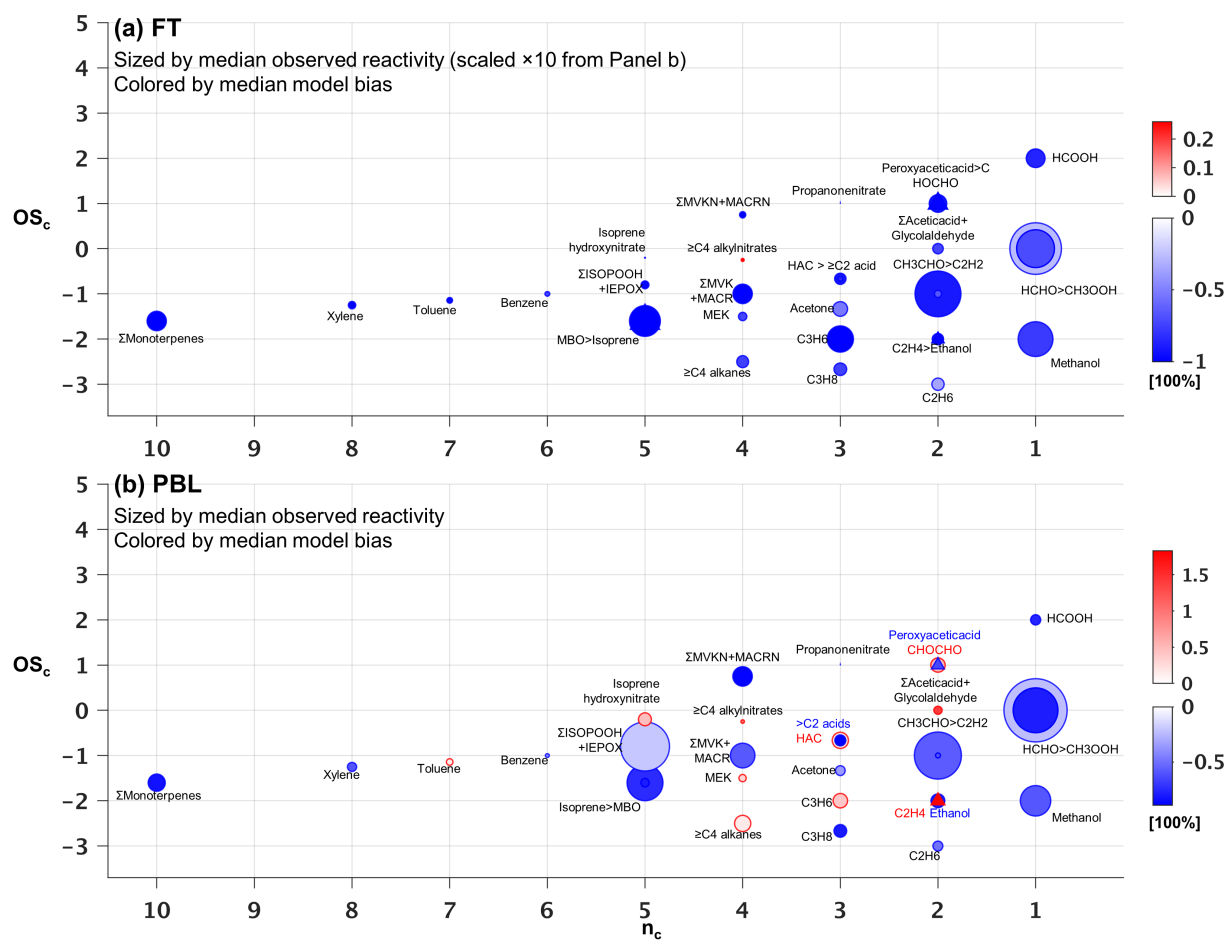


Figure S9. Same as Figure 6, but with the color shaded indicating the median relative model bias. Note that the relative model bias in VOC-carbon for a given species is identical to that for OH reactivity, except in the case of lumped or co-measured species.

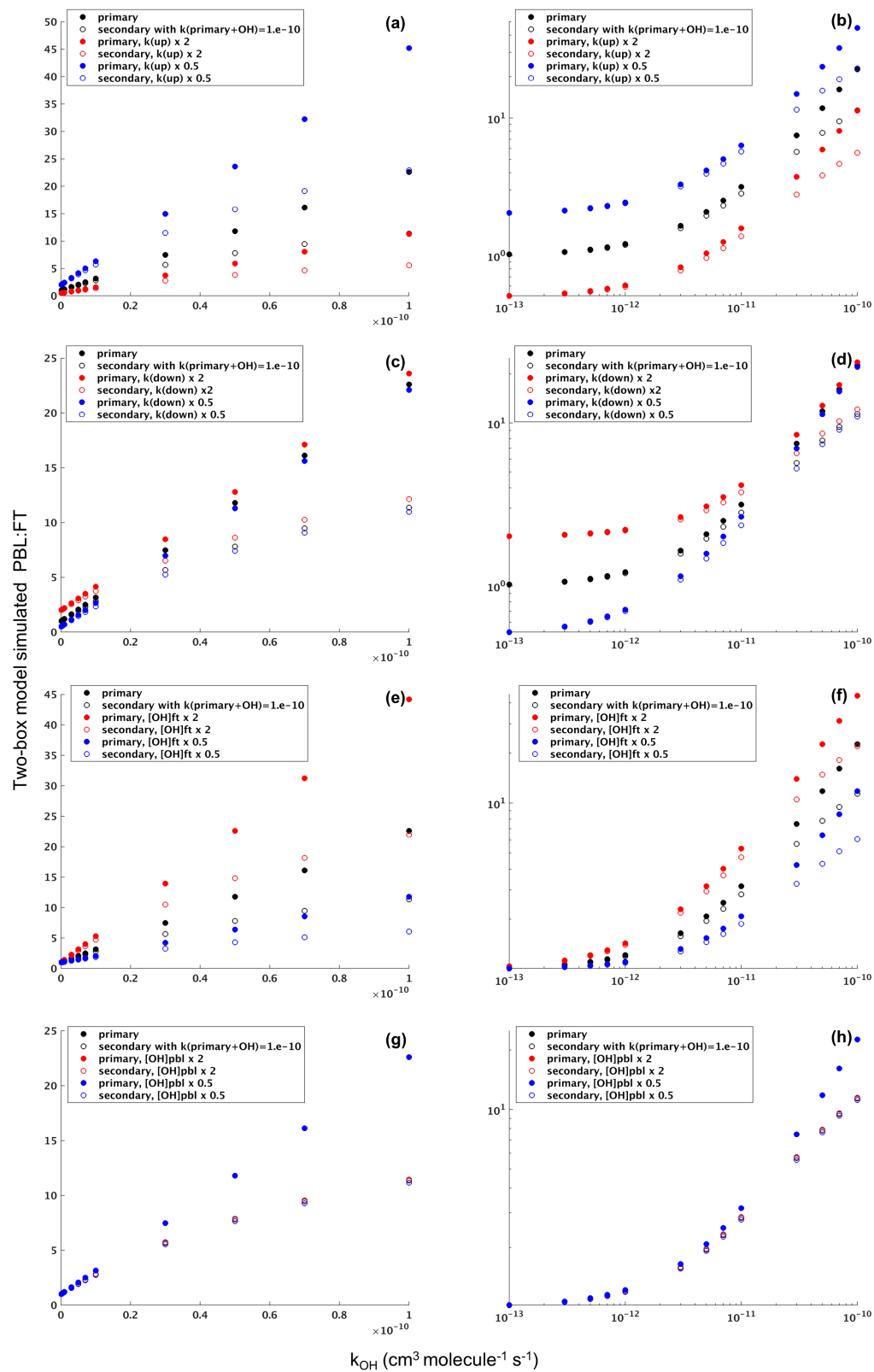


Figure S10. Sensitivity of the PBL:FT concentration ratio for primary and secondary VOCs to PBL-FT exchange rates, OH, and reactivity, based on a simple two-box model. See main text.

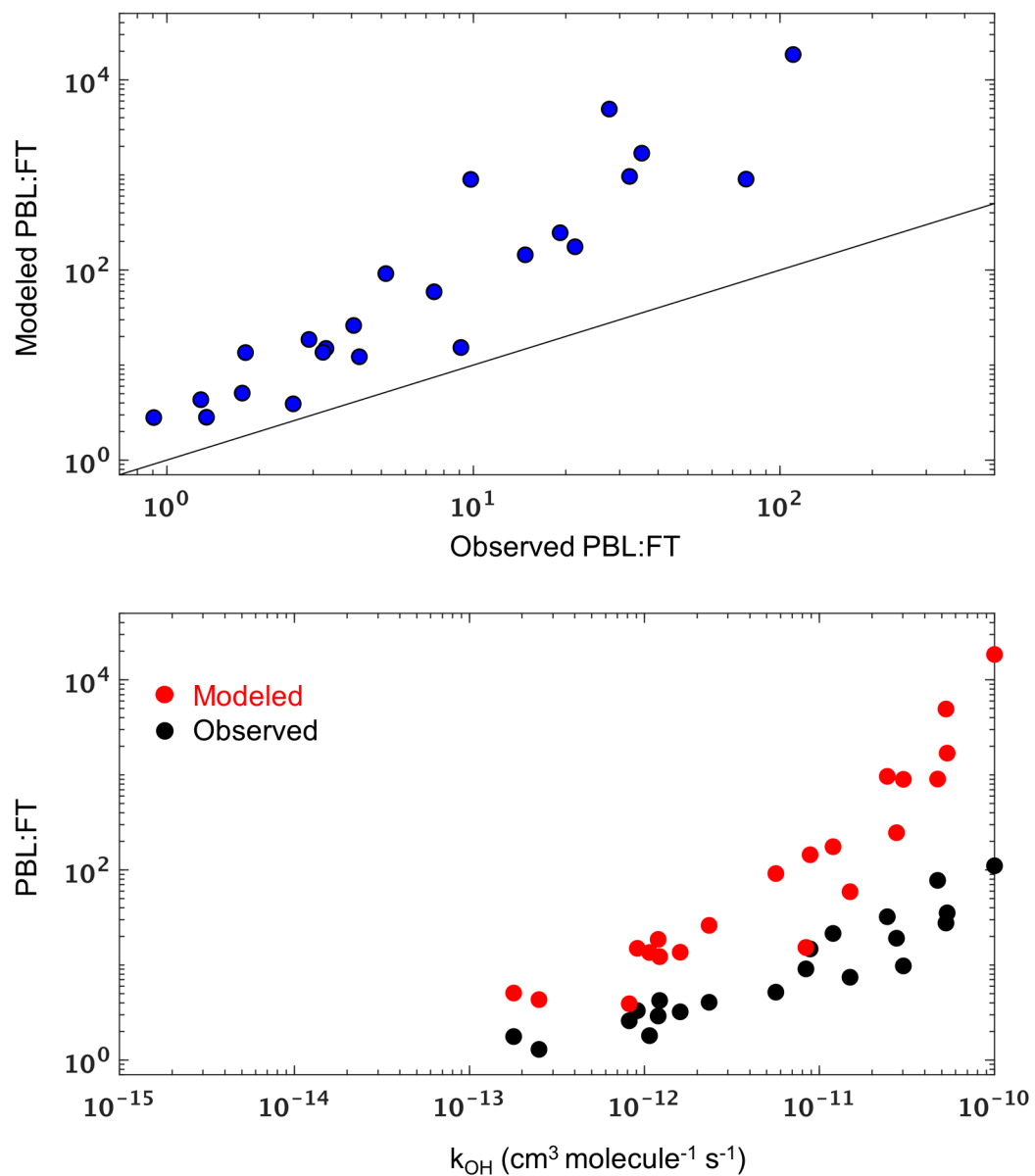


Figure S11. Same as Figure 9, but with model results from a sensitivity simulation with 40% reduced PBL depths.

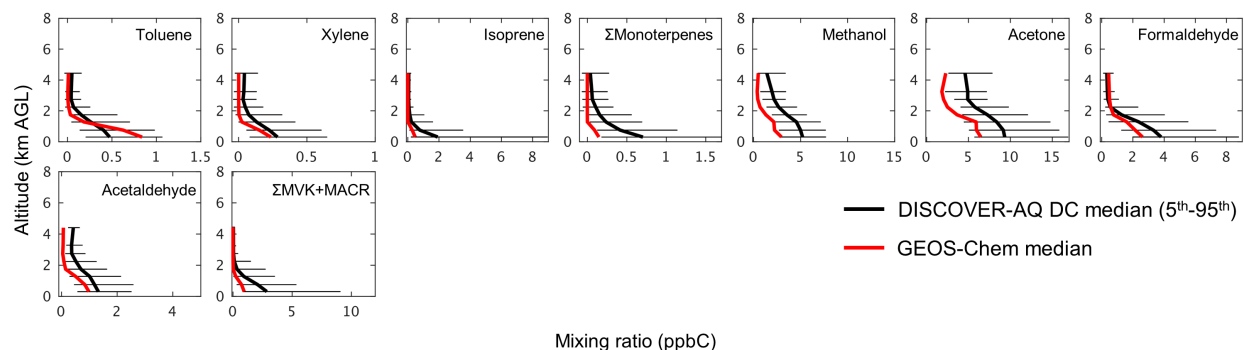


Figure S12. Vertical VOC profiles as measured and simulated by GEOS-Chem during the DISCOVER-AQ DC aircraft campaign. Plotted are the observed (black) and predicted (red) median profiles (in ppbC), with horizontal bars indicating the 5th - 95th percentiles measured for each bin. The vertical bin resolution is 0.5km below 3km and 1km above 3km. Fresh biomass burning and pollution plumes have been filtered out as described in-text.

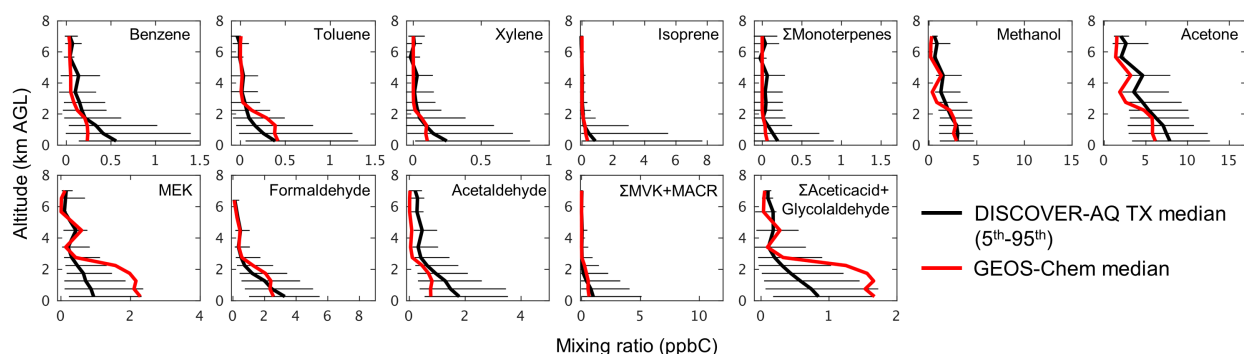


Figure S13. Same as Figure S5 but for the DISCOVER-AQ TX aircraft campaign.

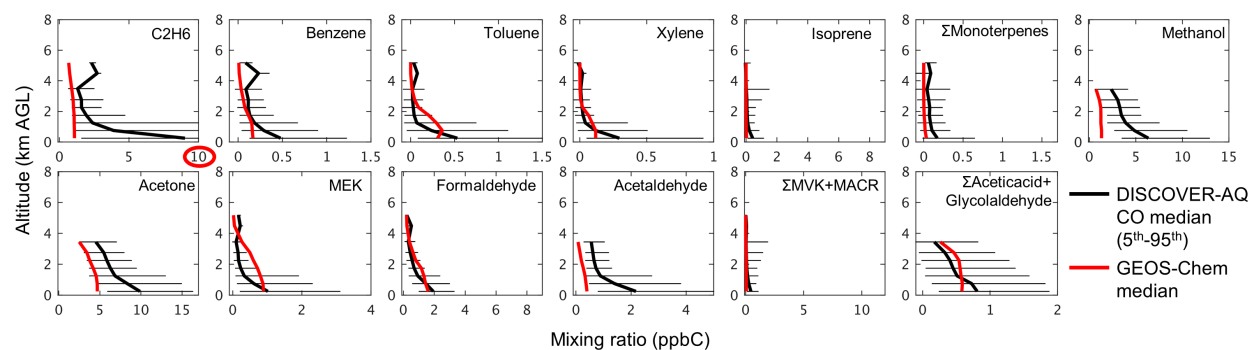


Figure S14. Same as Figure S5 but for the DISCOVER-AQ CO aircraft campaign. Red circles indicate axis scales that differ from others for the same compound in Fig. S5, 6, 9, 10.

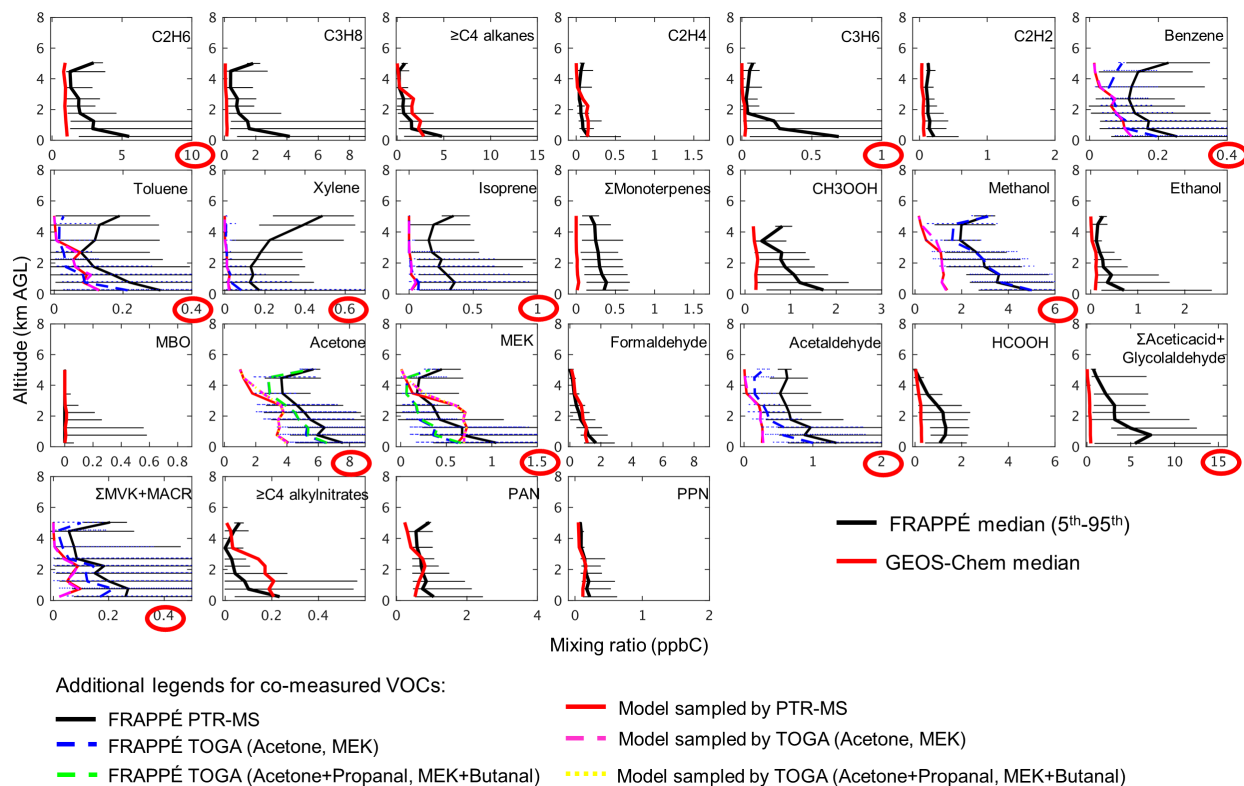


Figure S15. Same as Figure S5 but for the FRAPPÉ aircraft campaign. Red circles indicate axis scales that differ from others for the same compound in Fig. S5, 6, 9, 10.

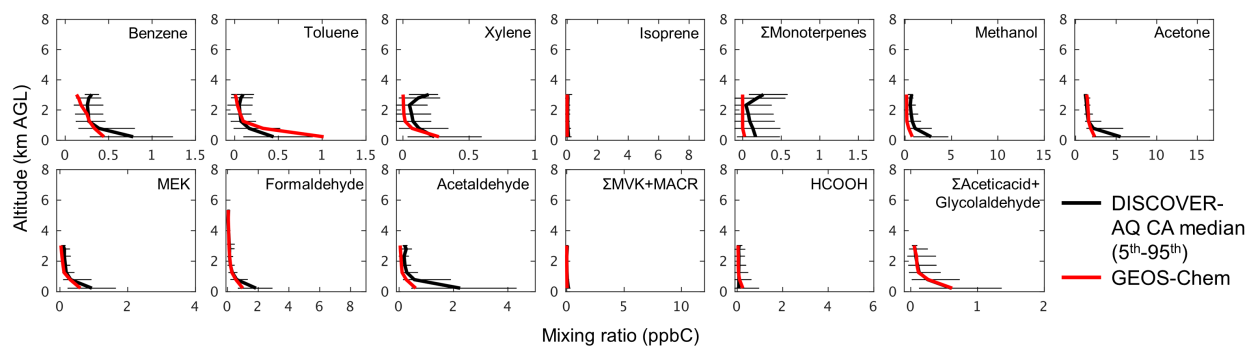


Figure S16. Same as Figure S5 but for the DISCOVER-AQ CA aircraft campaign.

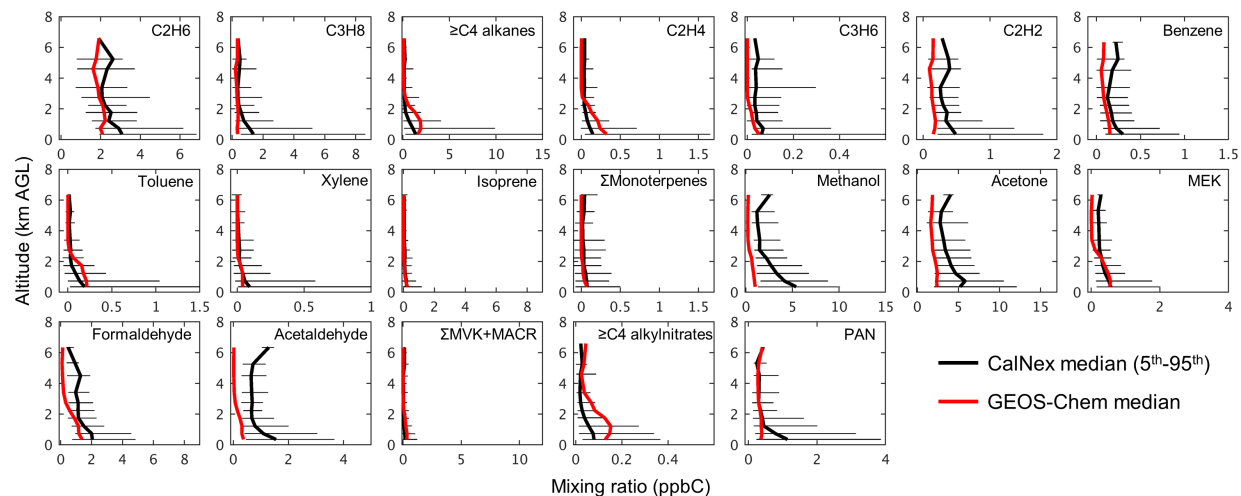


Figure S17. Same as Figure S5 but for the CalNex aircraft campaign.

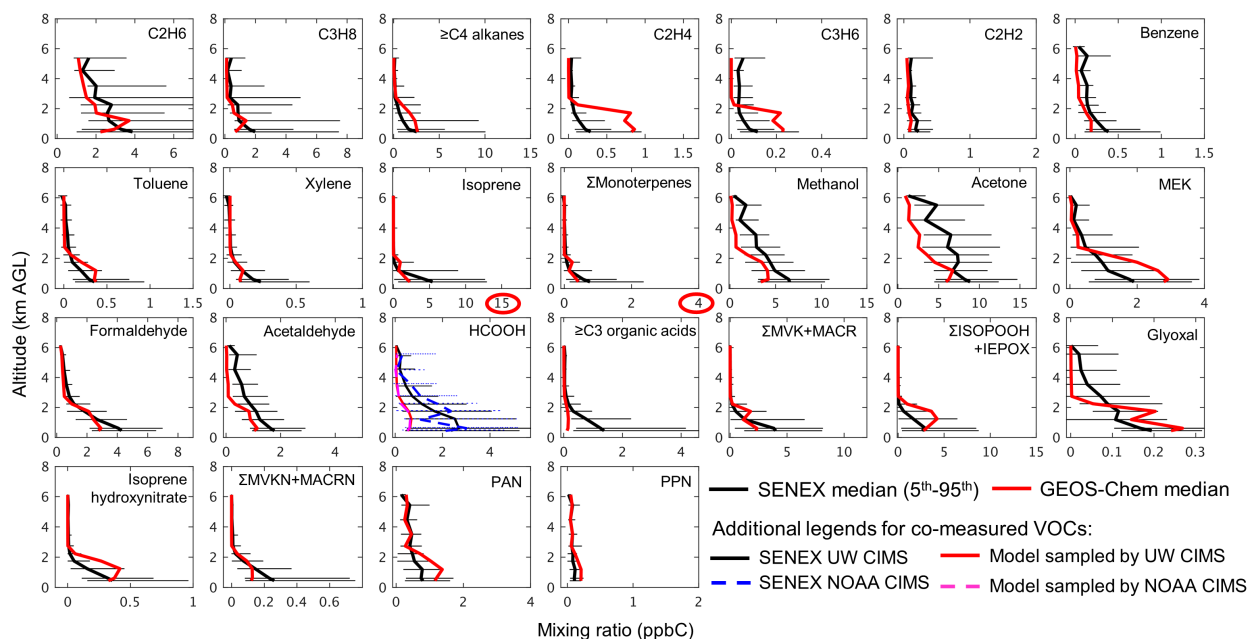


Figure S18. Same as Figure S5 but for the SENEX aircraft campaign. Red circles indicate axis scales that differ from others for the same compound in Figures S5, 6, 9, 10.

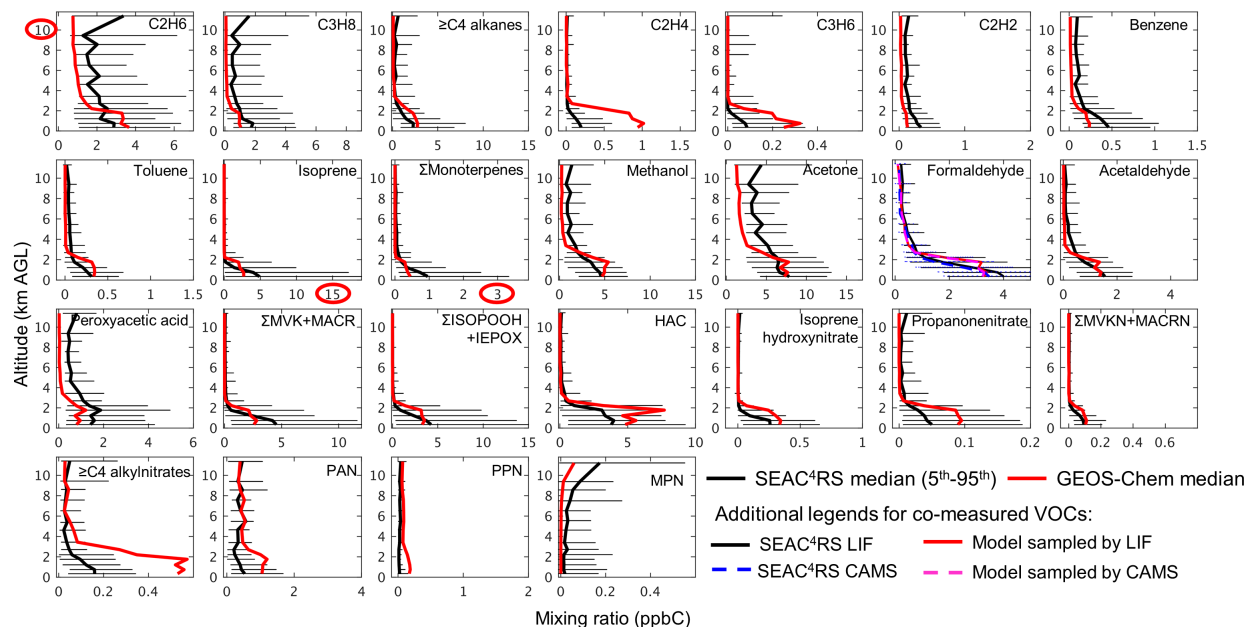


Figure S19. Same as Figure S5 but for the SEAC⁴RS aircraft campaign. Red circles indicate axis scales that differ from others for the same compound in Figures S5, 6, 9, 10.

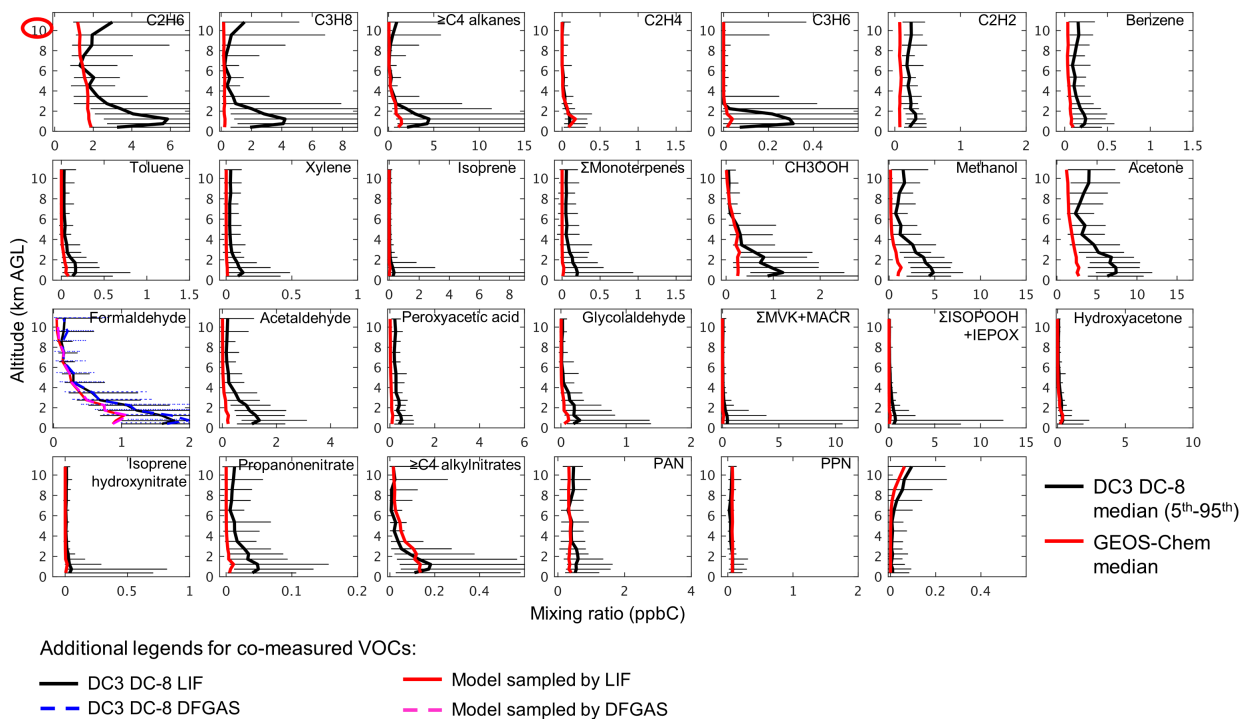


Figure S20. Same as figure S5 but for the DC3 DC-8 aircraft observation. Red circles indicate axis scales that differ from others for the same compound in Figures S5, 6, 9, 10.

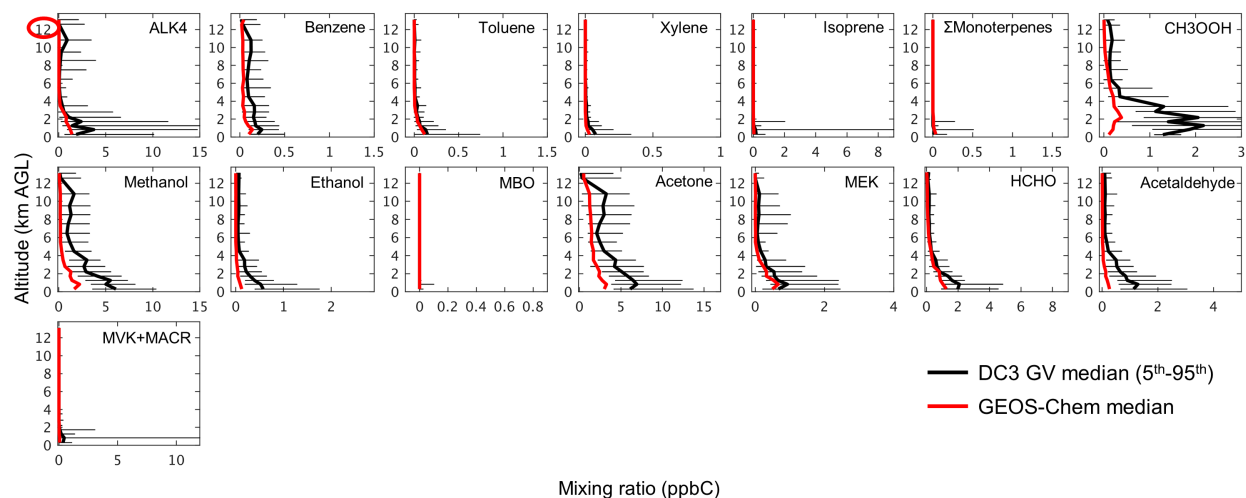


Figure S21. Same as figure S5 but for the DC3 GV aircraft observation. Red circles indicate axis scales that differ from others for the same compound in Figures S5, 6, 9, 10.

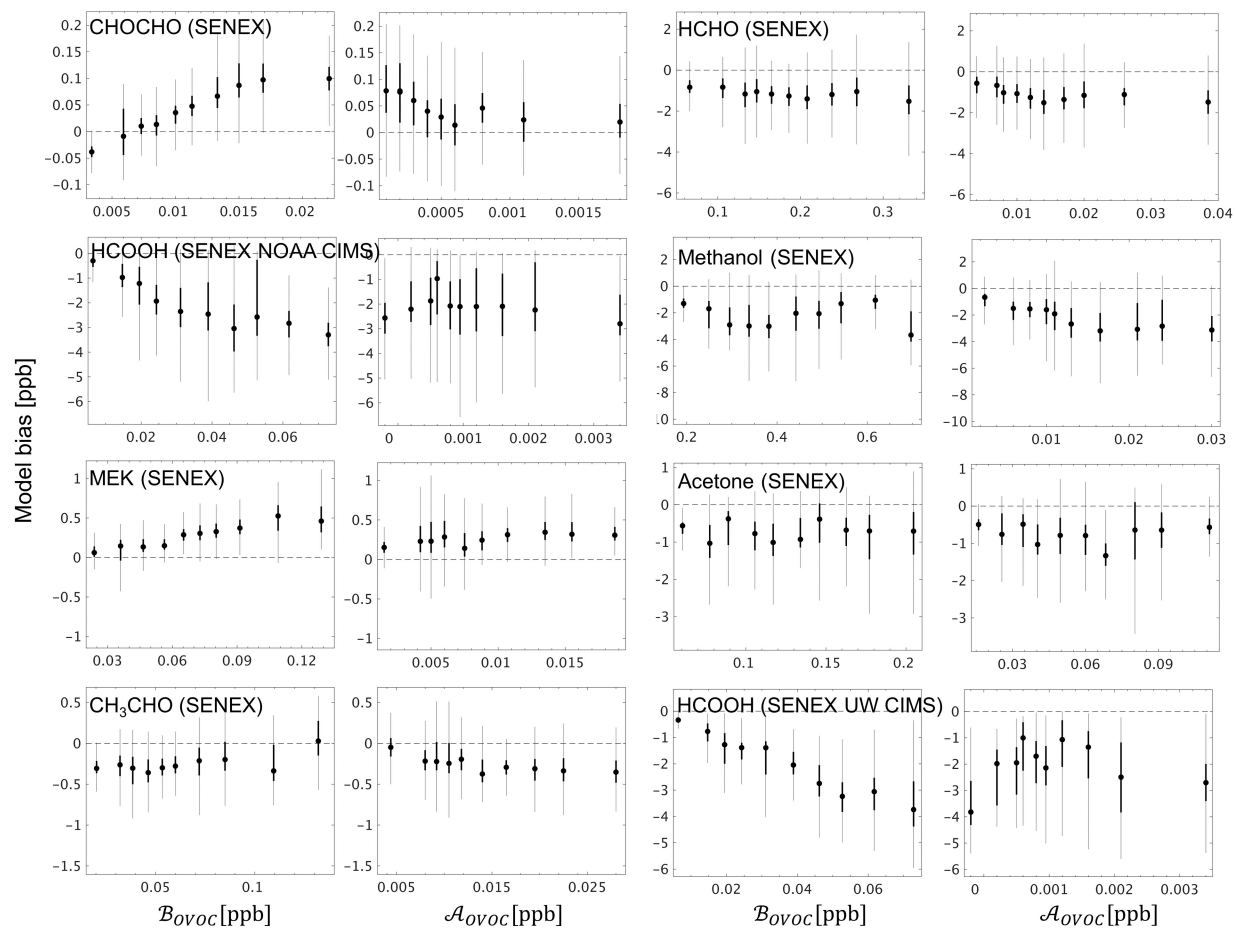
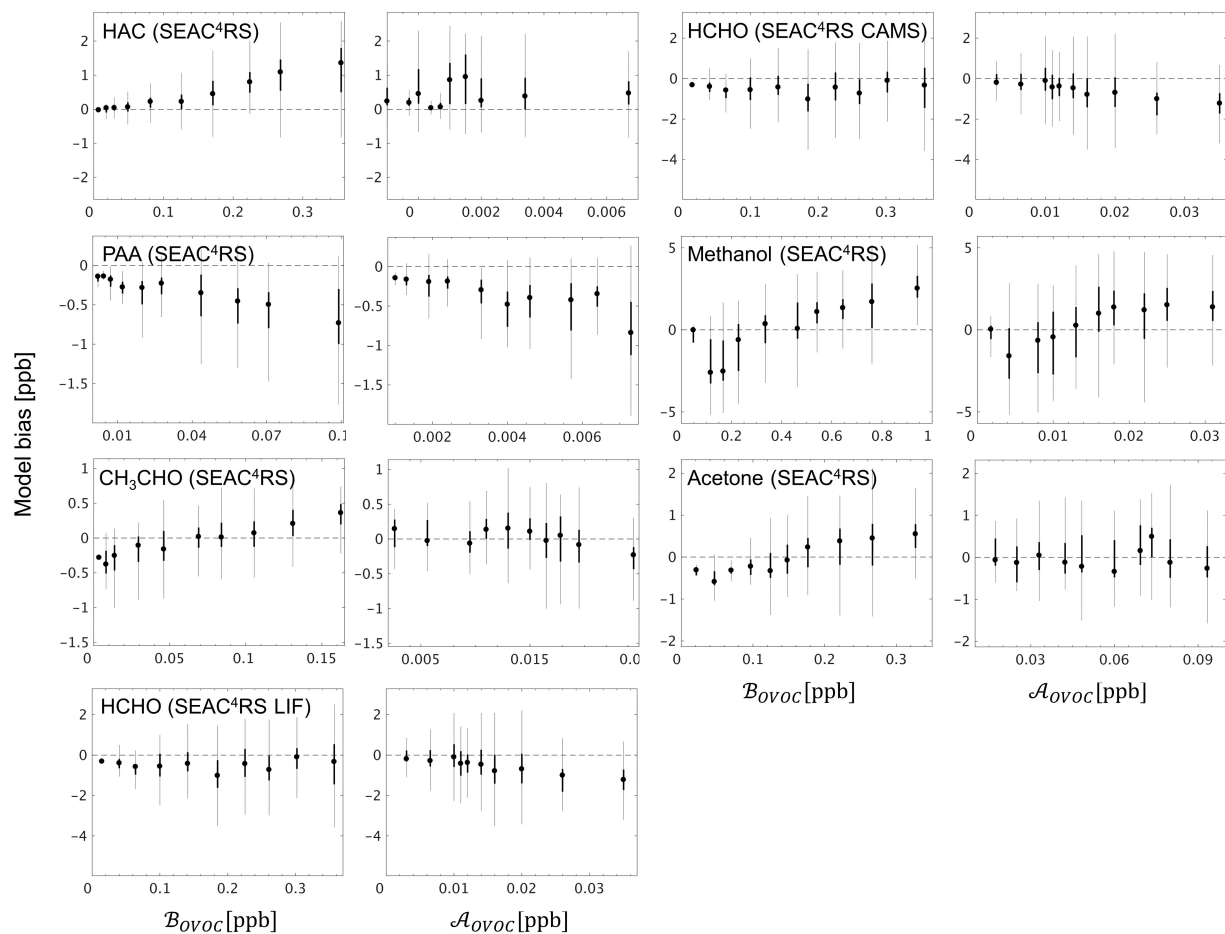


Figure S22. Same as Figure 10 but for the SENEX campaign.



131

132 **Figure S23. Same as Figure 10 but for the SEAC⁴RS campaign.**

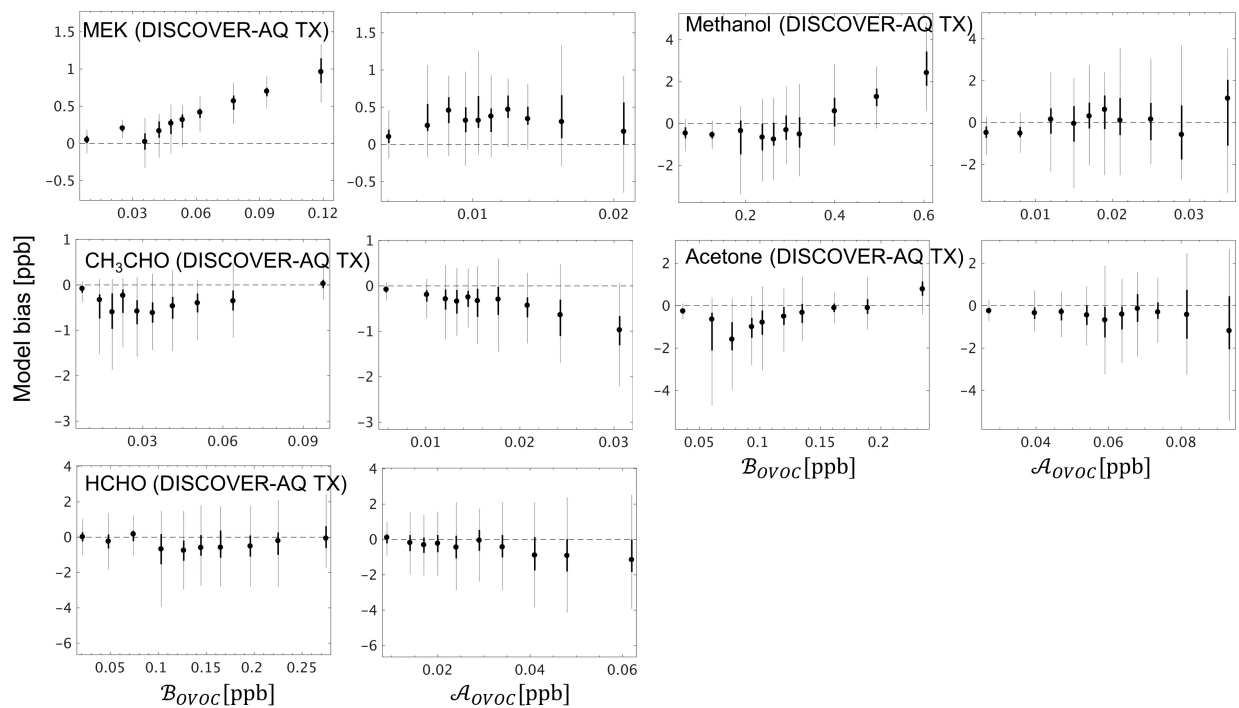


Figure S24. Same as Figure 10 but for the DISCOVER-AQ TX campaign.

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